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INSTABILITIES IN FREE RADICAL POLYMERIZATION

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ABSTRACT

The rheokinetics of bulk free radical polymerization has so far been investigated only at low degrees of conversion, where the system may be considered as Newtonian. In that case the rheokinetic equations can be linearized, yielding a simplified expression of the viscosity increase as a function of time during polymerization. In this paper we extend the rheokinetic approach to the study of bulk free radical polymerization at high degrees of conversion, where the rheokinetic equations may not be linearized and the system must be considered as non-Newtonian. Moreover, the occurrence of the so-called gel effect complicates the nonlinearity of the rheokinetic problem even more.

The rheokinetic experiments performed show that the gel effect is reduced when the polymerization is performed at high shear rates. At very high degrees of conversion an onset of irregularities in the viscosity measurements was noticed. Possible explanations for these irregularities are discussed.

Keywords: Rheokinetics, Gel effect, Polymerization, Shear

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1. INTRODUCTION

The kinetics of polymerization and the rheological behavior of polymeric systems are often two separate fields of research. In fact, researchers focus most times on only one of those two very important aspects of polymer technology. Nevertheless, the dramatic increase of viscosity during a polymerization can influence the kinetics of polymerization. This happens, for example, when the polymerization becomes diffusion controlled because the movement of the macromolecules is hindered by the increasing viscosity.

Therefore, a new field of research, called rheokinetics, has been developing in recent years. Rheokinetics is the study of the changing rheological behavior of polymerizing systems aimed at a more complete understanding of the kinetics of the polymerization. Several papers appeared in the literature regarding rheokinetics [1-5] but they mainly concern low degrees of conversion. In this paper we try to extend the rheokinetic approach at high degrees of conversion.

2. LINEAR AND NONLINEAR RHEOKINETICS

In the case of bulk free radical polymerization the viscosity can be expressed as follows:

$$\eta = kN^a \beta^b \tag{1}$$

where η is the viscosity, N is the number-average degree of polymerization and β is the concentration of polymer; k, a and b are constants

If chain transfer reaction can be neglected, N and β are described by the following expressions:

$$N = \frac{[M_0]\beta}{[I_0](1-e^{k_i t})} \tag{2}$$

$$\ln(1-\beta) = \frac{2f^{1/2}k_p}{k_i^{1/2}k_t^{1/2}}[I_0]^{1/2}(1-e^{-k_i t}) \tag{3}$$

where $[M_0]$ and $[I_0]$ are the initial concentrations of monomer and initiator, f is the efficiency factor of the initiation reaction and k_i, k_p and k_t are the rate constants of the initiation, propagation and termination reaction, respectively.

By substituting (2) and (3) into (1), it is possible to derive the following expression that predicts the increase of viscosity with time during a bulk free radical polymerization.

$$\eta = K[M_0]^a[I_0]^{-a}\left[1-\exp\left(-\frac{2f^{1/2}k_p}{k_i^{1/2}k_t^{1/2}}[I_0]^{1/2}(1-e^{-k_t t})\right)\right]^{(a+b)} \quad (4)$$

A simplified version of (4) can be obtained expanding (2) and (3) into power series until the linear terms (for $\beta<<1$ and $k_i t<<1$) and then substituting in (1). The following relationship is then obtained:

$$\eta = \Theta_1 t^b \quad (5)$$

where

$$\Theta_1 = K[M_0]^a\left(\frac{k_p}{k_0^{1/2}}\sqrt{2f}\right)^{a+b}(k_i[I_0])^{1/2(b-a)} \quad (6)$$

In the rheokinetics studies performed so far, this simplified expression has been used, which is valid only at low degrees of conversion. Therefore the polymerizing fluid could be considered as Newtonian and the influence of shear rate on the viscosity could be neglected.

Notwithstanding these strong limitations, it was possible to predict successfully with (5) the increase of viscosity in the early stages of the polymerization, solving the so-called direct rheokinetic problem. On the other side, it was also possible to calculate some kinetic parameters, as the rate constants and the activation energies, by measuring the viscosity increase and using the rheokinetic model.

When considering the whole polymerization in the rheokinetic study, the fluid must be considered non-Newtonian and therefore it must be taken into account that all the parameters involved in the rheokinetic model might depend on the shear rate.

Moreover, the simplified version (4) of the rheokinetic equation may not be considered. The rheokinetic study becomes therefore a complicated nonlinear problem.

3. MATERIALS AND METHODS

Styrene and n-buthylmthacrylate (BMA) were purchased and used without any further purification. The radical initiator was Trigonox 42S. The concentration of radical initiator was 0.33% v/v.

The viscosity measurements were performed at constant shear rate and constant temperature with a cone and plate rheometer (Brabender Co., Duisburg, Germany). The diameter of the cone was 50 mm, the angle 3°. The rheometer is provided with a thermostating bath and a temperature control system.

4. RESULTS AND DISCUSSION

The viscosity increase during the bulk free radical polymerization of styrene and BMA was measured in different experimental conditions at constant temperatures in the range 90-115°C and constant shear rates in the range 6-400 s^{-1}. The trend was in all cases qualitatively the same. One example is shown in fig. 1.

The data can be fitted by a double power law curve. The exponent of the second part of the curve is always higher than the exponent of the first part. This denotes that at a certain point the viscosity increase becomes faster. In other words, the gel effect [6] sets in. The difference between the two exponents can be considered as a measure of the gel effect.

The transition point between the two power law curves has been determined optimizing the fit in order to have the highest possible regression parameter. The degree of conversion corresponding to the transition point has been determined by NMR and resulted to be 65%. Anyway this value must be considered as a qualitative indication of the conversion at the onset of the gel effect. The latter, in fact, does not take place suddenly at a certain time and at a certain conversion, but sets in gradually.

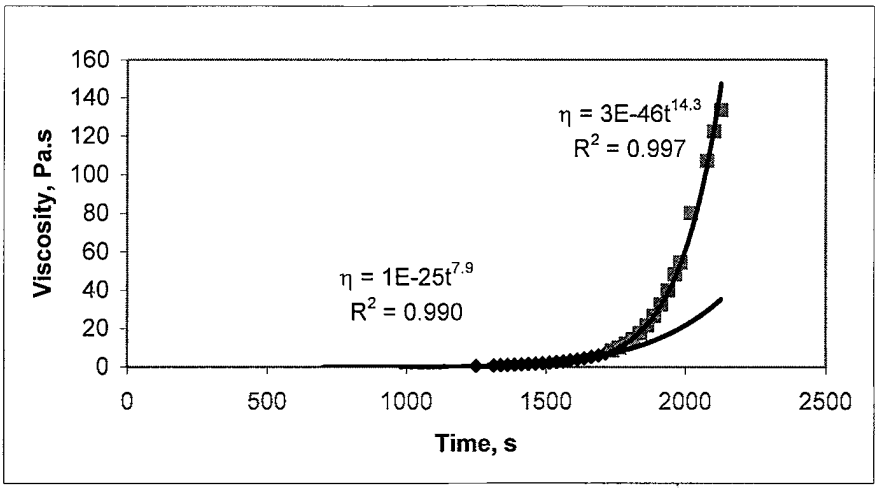

Fig.1. The increase of viscosity during the polymerization of BMA. T=90°C; shear rate = 30 s^{-1}.

The results of experiments performed at different shear rates, but at the same temperature have been compared plotting the two power law exponents as a function of the shear rate at which the polymerization is performed . Once again, it was always obtained a similar qualitative trend. Two examples are shown in fig. 2 and 3.

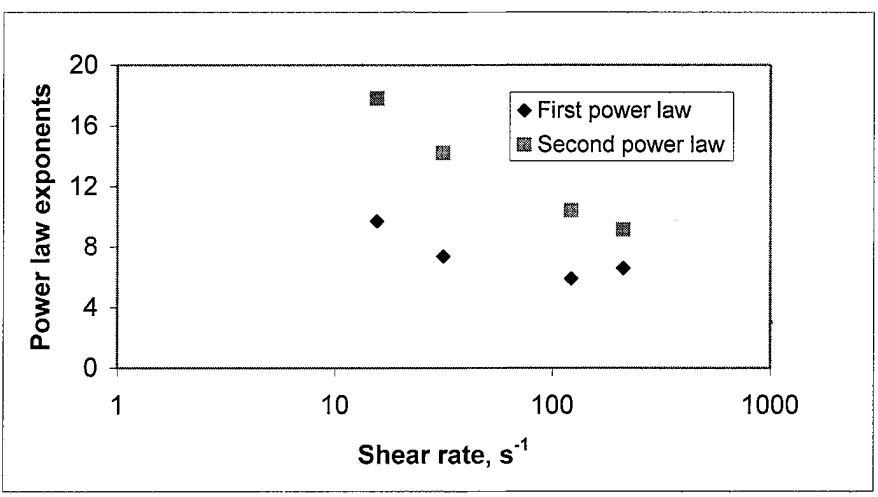

Fig. 2. Power law exponents as a function of shear rate for the polymerization of BMA at 110°C.

It is evident that the difference between the two power law exponents decreases if the polymerization is carried out at a higher shear rate. When the shear rate is 400 s^{-1}, the viscosity increase can also be fitted by a single power law (data not shown).

This fact means that the gel effect, and its negative consequences [7], can be significantly reduced, if not eliminated, in high shear flow conditions. Moreover the termination rate constant k_p results to depend on the shear rate: the higher the shear rate, the higher is k_p.

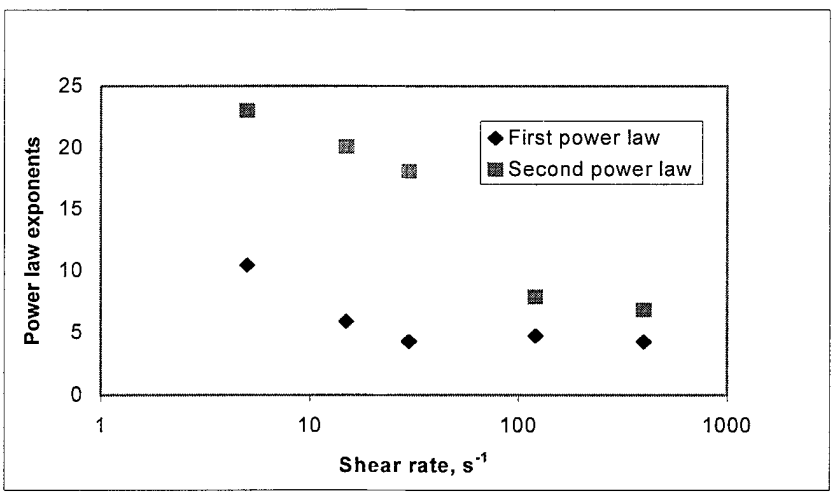

Fig. 3. Power law exponents as a function of shear rate for the polymerization of styrene at 90°C.

It can be argued that this reduction of the gel effect is due to the fact that at a high shear rate the macromolecules tend to orientate and elongate. In a similar situation the diffusion limitations, which are the underlying reason of the gel effect, are reduced because of the increased degree of order of the system.

Figure 1 refers only to the first part of the data obtained during a typical experiment. The complete data are plotted in figure 4.

After the regular and reproducible increase of the viscosity, a highly irregular and irreproducible trend sets in at a degree of conversion of about 85%. Repeating the same experiments many times no characteristic trend or periodical behavior could be noticed after the double power law increase of the viscosity. The only reproducible aspects were the presence and the onset of these irregularities.

The easiest explanation for this irregular and irreproducible behavior could be a failure of the cone and plate rheometer. However, this hypothesis must be ruled out because a common value for all the experiments of the measured shear stress (the viscosity is then calculated dividing the shear stress by the shear rate) could not be noticed.

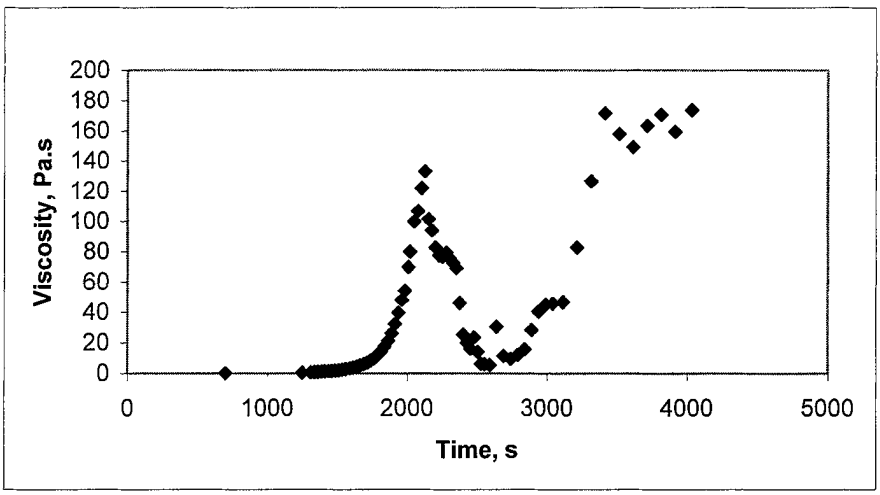

Fig. 4. The increase of viscosity during the polymerization of BMA.T=90°C; shear rate = 30 s^{-1}.

Also the possibility of slip between the sample and the cone and/or the plate can be ruled out. In fact, the experiments were also occasionally repeated with radially grooved cone and plate and the same result were obtained qualitatively: a regular double-power-law trend of the viscosity increase followed by irregular oscillations. A quantitative comparison with the data obtained with the standard cone and plate was not possible because the smoothness of the surfaces is essential for a precise viscosity measurement.

A possible explanation for the irregularities in the measurements is the occurance of some non-homogeneity in the reaction mixture brought about by the shear. Local concentrations of polymer molecules will leave the rest of the mixture less viscous as seen by Malkin and Kulichikhin [8], who noticed a decrease in viscosity for polymerizing systems when phase separation occurred and by Onuki [9], who came to

similar conclusions performing computer simulations. Also other authors [10-13] studied shear-induced phase separations for polymer solutions.

This presumed non-homogeneity may be conventional thermodynamically driven phase separation, or some transient formation of a thermodynamically unstable pseudo-phase. In any case, it seems to be enhanced by a high shear rate. In fact, the maximum viscosity of the regular and reproducible trend show a remarkable dependence on the shear rate at which the polymerization is carried out. A typical example is presented in figure 5. The data are well fitted by a single power law trend, whose exponent is lower than –1. In other words, the phenomena under investigation can not be simply attributed to a shear thinning behavior.

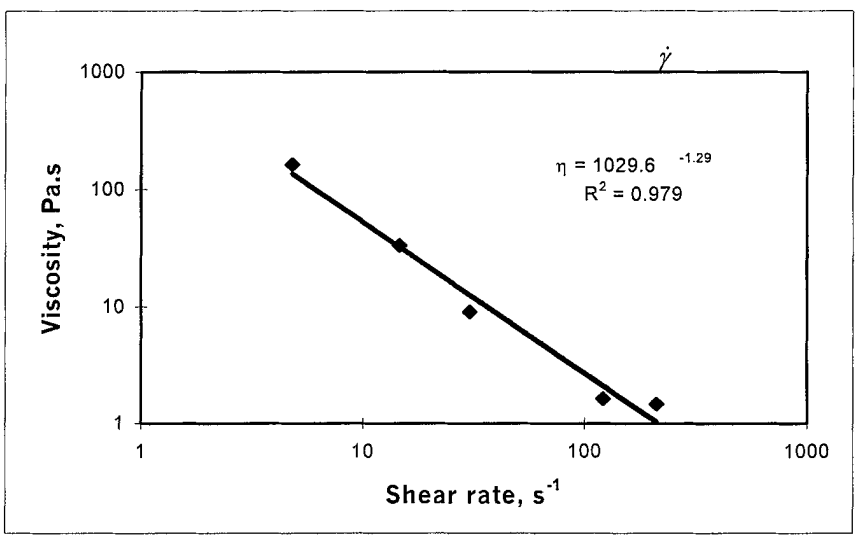

Fig. 5. Maximum shear stress for the polymerization of styrene at 90°C.

As in the case of the reduction of the gel effect, it can be argued that the increasing shear rate induces a higher degree of order in the system or, in other words, a decrease of the entropy of the system. Therefore the chemical potential increases, perhaps even resulting in a driving force towards phase separation when the polymeric system is sheared at high rates [14].

Unfortunately, it was not possible to test experimentally if phase separation takes place with a microscope technique. The phenomena under investigation are induced by the

shear. They are therefore very difficult to study, for instance by microscopy since the effect would be lost when taking a sample and preparing it for microscope analysis.

5. CONCLUSIONS

The rheokinetics of free radical polymerization has been studied at intermediate and high degrees of conversion. Particular attention has been devoted to the influence of the shear rate on the viscosity increase during the polymerization.

The rate constant of the termination reaction resulted to be dependent on the shear rate.

The gel effect is reduced, if not eliminated, when the polymerization is performed at higher shear rate.

Instabilities arise at high degrees of conversion and are ascribed to occurrence of inhomogeneities in the polymerizing fluid induced by the shear.

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